Name:__________________ SID:__________________ TA: Michele or Henry

Exam #2

Biophysical Chemistry

Chemistry 130A

Fall 2002

Justify all your assumptions!

Show <u>all</u> your calculations!

Make sure all your conclusions are physically reasonable.

Keep track of units and significant digits!

Underline or Box all your final answers!

Keep you answers brief!

Exams in pencil won't be regraded.

Questions	***Points***	***Score***
1		
2		
3		
4		
5		
6		
7		
Total		

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Information Page

$$R = 8.3145 \text{ J/(K mol)} = 0.08206 \text{ L atm / (K mol)}$$

$$F = \text{Faraday's constant} = 9.6485 \times 10^4 \text{ C/mol}$$

$$\log(\gamma) = -0.509\, Z\iota\sqrt{\mu}$$

Oxidant/Reductant	Electrode Reaction	Reduction Potentials	
		ε° (V) Chemist's standard state	$\varepsilon^{\circ\prime}$ (V) Biochemist's standard state
$NAD^+/NADH$	$NAD^+ + H^+ + 2e^- \rightarrow NADH$	-0.105	-0.320
$H^+/H_2/Pt$	$2\,H^+ + 2\,e^- \rightarrow H_2(g)$	0.0	-0.421
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag(s)$	0.799	
Fe^{2+}/Fe	$Fe^{2+} + 2\,e^- \rightarrow Fe(s)$	-0.4402	
$0_2/H_2O$	$\frac{1}{2}\,O_2 + 2\,H^+ + 2e^- \rightarrow H_2O$	1.23	0.82
$FAD^+/FADH_2$	$FAD^+ + 2H^+ + 2e^- \rightarrow FADH_2$		-0.219

Reaction	$\Delta G^{\circ\prime}$ kJ/mol
D-Glucose -6-Phosphate $\rightarrow$ D-Fructose-6-Phosphate	1.7
Pyruvate + NADH + $H^+ \rightarrow$ Lactate + NAD^+	-25.1
ATP + $H_2O \rightarrow$ ADP + Phosphate	-31.0
2-Phosphoenolpyruvate + ADP $\rightarrow$ Pyruvate + ATP	-31.4

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1. Short Questions

(a) If we double the volume of a mole of ideal gas, the change in entropy is Rln(4).

TRUE $\boxed{\textbf{FALSE}}$

(b) It is possible for a process to from A to B to proceed if the process is both exothermic and exentropic (increased entropy)?

$\boxed{\textbf{TRUE}}$ **FALSE**

(c) A plot of ln(K) versus 1/T has a positive slope for an endothermic reaction.

TRUE $\boxed{\textbf{FALSE}}$

(d) The reaction A → 2 B is known to occur. Upon measuring a solution which has just been prepared in the laboratory with 1 mole of A and 2 moles of B, it is found that μ_A= 4.8 J/mol and μ_B= 2.4 J/mol. What is true about the solution?

(a) More reactants will form.
(b) More products will form.
$\boxed{\text{(c) The reaction is in equilibrium, so there will be no change in amount of products or reactants.}}$
(d) There is not enough information to tell.

2. pH Buffers

Calculate the pH of the following solutions:

a) 10^{-3} M of H_2CO_3 in water (K_1=4.35*10^{-7}M, K_2=4.69*10^{-11}M)

For the first dissociation:

$4.35*10^{-7} = x^2/(10^{-3} - x)$ → Assume x<< 0.001 or solve the quadratic equation

x~= 2.06*10^{-5} (which *is* less than 0.001 by a good bit)

So pH is ~4.68.

For the second: $4.69*10^{-11} = y^2/(x - y)$ → y~= 3.12*10^{-8} << x

b) The same solution as in (a) plus 10^{-3} M of $NaHCO_3$

Following the same logic as before but adding in the extra HCO_3^+

$4.35*10^{-7} = x(0.001+x)/(10^{-3} - x)$→x~= 2.13*$10^{-7}$ → pH~= 6.67

c) The same solution as in (a) plus 10^{-1} M of Na_2CO_3

Here we are adding a good bit of base….

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3. Common Ion Effect

The solubility product, K_{sp}, of AgCl is $1.6*10^{-10}$

a) Find the concentration of a saturated Ag^+ in water solution (AgCl fully dissociates).

$AgCl(s) \rightarrow Ag^+ + Cl^-$

$K_{sp} = [Ag^+][Cl^-] = 1.6 * 10^{-10} = x^2 \rightarrow x = [Ag^+] = 1.26*10^{-5}$ M

b) Find the concentration of Ag^+ in a saturated water solution containing 1M NaCl.

$AgCl(s) \rightarrow$	Ag^+ +	Cl^-
Solid	**x**	**(1+x)**

$1.6 * 10^{-10} = x(1+x) \sim= x = [Ag^+]$ (since $x^2 << x$)

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4. Simple Redox

Show all reactions and calculations for each question. Remember Faraday's constant is 98,494 C/mol

a) Can NADH be used to reduce $FADH_2$? Write the reactions you use for the calculation.

$FAD^+/FADH_2$	$FAD^+ + 2H^+ + 2e^- \rightarrow FADH_2$	$\varepsilon°' = -0.219$
$NAD^+/NADH$	$NAD^+ + H^+ + 2e^- \rightarrow NADH$	$\varepsilon°' = -0.320$

Subtracting the bottom reaction from the top gives $\varepsilon°'_{cell} = 0.101$ V . A the biochemist's standard state NADH will reduce FAD^+

b) Can O_2 be used to oxidize NADH? How many ATP molecules can be synthesized by this reaction?

$0_2/H_2O$	$\frac{1}{2} O_2 + 2 H^+ + 2e^- \rightarrow H_2O$	1.23	0.82

Subtracting the NAD^+ reaction from the above reaction gives $\varepsilon°'_{cell} = 1.24$ V. So it will work.

$\Delta G° = -nF\varepsilon° = -220$ kJ/mol → # of ATP's synthesized= 220 kJ/mol / (31 kJ/mol)= 7 molecules of ATP.

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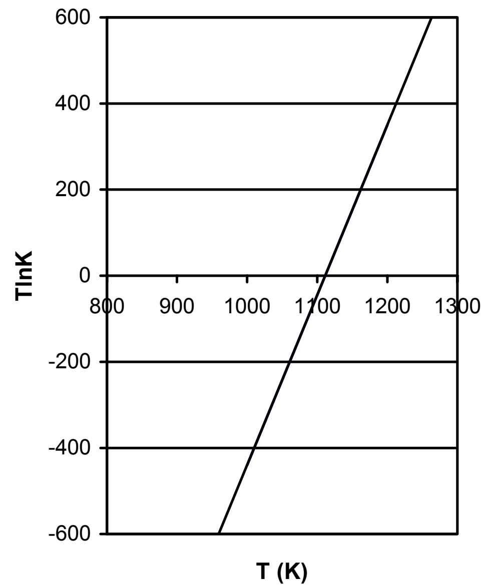
5. Temperature dependence.

An unusual form of plotting temperature variation of the equilibrium constant of a reaction is shown to the right. Calculate ΔG°, ΔH°, ΔS°, and K at 1200 K.



At 1200 K from graph, TlnK ≈ 350 ⇒ **ΔG°** = −RTlnK = −(8.31)(350) = **−2.91 kJ/mol**.

$$\ln K = 350/1200 = 0.29 \Rightarrow \mathbf{K = 1.3}$$

Since the y-axis is TlnK, this is a plot of −ΔG°/R vs. T.

From dG = −SdT + VdP ⇒ $(\partial G/\partial T)_P = -S$. Therefore the slope of this plot is ΔS°/R.

Slope = Δy/Δx = [350 − (−440)] / [1200 − 1000] ≅ 4.0 = ΔS°/R ⇒ **ΔS° = 33 J/mol∗K**.

ΔG° = ΔH° − TΔS° ⇒ **ΔH°** = ΔG° + TΔS° = (-2.91×10^3) + (1200)(33) = **37 kJ/mol**.

6. **More temperature**

The standard enthalpy of a certain reaction is 125 kJ/mol over a wide temperature range. If the standard Gibbs free energy for this reaction at 1300 K is 33 kJ/mol, estimate the temperature at which the equilibrium constant, K, becomes greater than 1 (i.e. when $0 \geq \Delta G°$).

$\Delta G° = -RT \ln K \Rightarrow \mathbf{K_{1300}} = e^{-\Delta G/RT} = e^{-[33{,}000/(8.314*1300)} = \mathbf{0.0472}$

$\ln K_2/K_1 = -\Delta H°/R\ (1/T_2 - 1/T_1) \Rightarrow K_2 = 1$ for the lower limit of T_2

$\ln 1 - \ln 0.0472 = -(125{,}000/8.314)*(1/T_2 - 1/1300) \Rightarrow \mathbf{T_2 = 1770\ K}$.

7. **LeChatelier's principle**

A mixture of nitrogen and oxygen at 2000 K reacts to form nitric oxide:

$$N_2 + O_2 \leftrightarrow 2\ NO \qquad K_a = 4.00 \times 10^{-4}$$

where K_a is the equilibrium constant calculated from the activities of the reactants and products.

a) What does Le Chatelier's Principle predict about this equilibrium if the total pressure is increased by decreasing the volume? Why?

Since $\Delta n = 0$, Le Chatelier predicts that increased pressure has **no effect** on the equilibrium.

b) Consider the same reaction at a total pressure of 2.0 kbar. If $\gamma(NO) = 1.21$, $\gamma(N_2) = 1.50$, and $\gamma(O_2) = 1.40$, calculate K_p (equilibrium constant calculated from the partial pressures of the reactants and products of the reaction).

$K_a = [(\gamma_{NO}P_{NO})^2] / [(\gamma_{N2}P_{N2})^* (\gamma_{O2}P_{O2})] = K_\gamma{}^*K_p \Rightarrow$

$\mathbf{K_\gamma} = (1.21)^2 / (1.50*1.40) = \mathbf{0.697} \Rightarrow \mathbf{K_p} = K_a/K_\gamma = (4.00 \times 10^{-4})/0.697 = \mathbf{5.7 \times 10^{-4}}$.

c) Does the result of part b) suggest a disagreement with Le Chatelier? If so, why? If not, why not?

Yes $\Rightarrow$ Since K_p at 2.0 kbar depends upon K_γ which varies with pressure, then K_p varies with P and therefore so does the relative values of the reactants and products at equilibrium.